Characteristics, Seasonality, Spatial Variation and Source Apportionment of Carbonaceous, Ionic and Metal Components in Fine Aerosols

A SYNOPSIS FOR THE AWARD OF THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

Submitted by

AWNI AGARWAL

Prof. K. MAHARAJ KUMARI

Supervisor

Prof. SAHAB DASS

Head, Department of Chemistry

Prof. RAVINDER KUMAR

Dean, Faculty of Science

DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
DAYALBAGH EDUCATIONAL INSTITUTE
(DEEMED UNIVERSITY)
DAYALBAGH, AGRA
(2015)

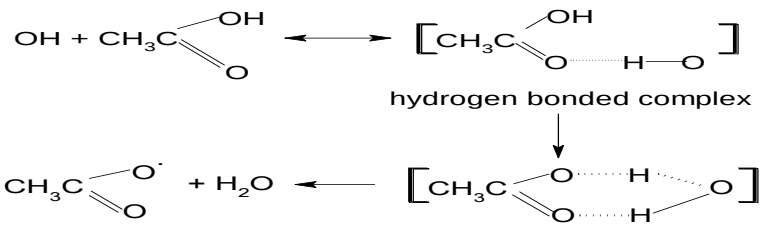
INTRODUCTION

Atmospheric air pollution in the present times has become a worldwide concern and therefore development of new control strategies has become essential in order to provide a sustainable environment for the future generations. The ever increasing energy demands have resulted in uncontrolled human activities and therefore a rise in pollutant concentration levels in different parts of the world. Atmospheric aerosols, among other pollutants, are important contributors of global air pollution. Aerosols may be defined as a suspension of solid or liquid particles in the air ranging from 10^{-9}-10^{-4}m. A vast number of environmental processes are influenced by the ubiquitous presence of aerosols in the atmosphere. Scattering and absorption of solar radiation by aerosols result in alterations in Earth's radiation balance of the atmosphere and cause significant climatic changes (Tiwari et al., 2015). A direct implication of this change in radiation balance is the uneven warming and cooling of the Earth's atmosphere by the aerosol constituents. As stated by IPCC, the global warming by greenhouse gases is counterbalanced by the overall cooling by aerosols which might be equivalent to a radiative forcing of up to -2.5Wm^{-2} (Gerasopoulos et al., 2006). Visibility impairment, changes in cloud and fog formation and precipitation are other related environmental effects of atmospheric aerosols. Effects of atmospheric aerosols are not only limited to the environmental degradation, but also extend to human health problems. Studies have confirmed that long term exposure to increased levels of $PM_{2.5}$ results in morbidity and mortality. Due to such environmental and health concerns, Particulate Matter (PM) is a much researched area of atmospheric chemistry. Based on the mass and composition, particulate matter can be distinguished into two distinct groups: coarse particles and fine particles. These particles have been divided based on their aerodynamic diameter. The coarse fraction of PM has an aerodynamic diameter of 10µm or less, while the fine fraction has a particle size of 2.5µm or less. The coarse fraction is also called the PM_{10} fraction while the fine fraction is referred to as $PM_{2.5}$. Particulate Matter (PM) originates from both natural as well as anthropogenic sources. Primary sources are emitted directly into the air while the secondary sources of PM involve homogeneous or heterogeneous reactions in air or

the gas to particle conversion processes. The coarse or the inhalable fraction of PM originates mainly from wind-blown dust from agricultural processes, uncovered soil, unpaved roads or mining operations, road dust, pollen grains, spores, sea spray, etc. Anthropogenic origin of PM_{10} includes fly ash from fossil fuel combustion. The fine or the respirable PM fraction, $PM_{2.5}$, come from gas and condensation of high-temperature vapours during combustion, fossil fuel combustion, vegetation burning, and the smelting and processing of metals. Due to their fine size and longer residence time compared to the coarse fraction, $PM_{2.5}$ is much extensively studied fraction of particulate matter. Being very small in size, $PM_{2.5}$ is capable of penetrating deep into the lung alveoli and adversely affects the human respiratory system. With the increasing levels of particulate pollution in ambient air, National Ambient Air Quality Standards (NAAQS) of India defined the $PM_{2.5}$ air quality standards as 60μgm^{-3} for 24h sampling periods. $PM_{2.5}$ is composed of a large number of individual compounds such as organic carbon (OC), elemental carbon (EC), ions, major and trace metals, etc. Carbonaceous aerosols constitute an important fraction of particulate matter. On annual basis, carbonaceous aerosols account for about 20-45% of $PM_{2.5}$ mass (Sandrini et al., 2014). It includes organic compounds and elemental or black carbon (soot). The elemental carbon (EC) and the organic carbon (OC) together make up the total carbon. Even though the two species are emitted from the same sources, they differ from each other in their physical, chemical and optical properties. Apart from CO_2 and methane, black carbon also absorbs large amount of solar radiation and thus contributes to warming up of atmosphere. On the other hand, organic carbon is associated with scattering of solar radiation. Recent studies support that OC emitted during biomass burning also contain a small component of humic-like substances, HULIS and Brown carbon, which absorb radiation at shorter wavelengths (Ram & Sarin, 2015). Black carbon is emitted from various sources which are mostly primary in origin. For instance, in the lower troposphere, the major emission sources of BC are fossil fuel and biomass burning at the surface. Aircraft engine exhaust is a source of BC in the upper troposphere and lower stratospheric region (Safai et al., 2012). Organic carbon is emitted from both primary and secondary sources. The secondary source of organic carbon is essentially the condensation of low vapour pressure compounds

which are emitted as primary pollutants or formed in the atmosphere (Sandrini et al., 2014). Organic fraction of atmospheric particulate matter is most difficult to characterize due to the variability in the chemical composition, sources which may be both local or long range transport and possible chemical transformations within the atmosphere.

Carboxylic acids are highly soluble in water and together with carbonyls, constitute an important fraction of total organic carbon. Formic acid and acetic acid form the dominant species of carboxylic acids and are most widely studied. Carboxylic acids play significant roles in controlling the acidity of rain water and are found to be associated with secondary organic aerosol formation. Secondary Organic Aerosols (SOA) are also formed as a result of gas to particle conversion process. In remote areas of the world, these two acids are found to contribute about 64% to the free acidity (Khare et al., 1999). Carboxylic acids are emitted primarily from automobile exhausts, vegetation, biomass burning, emission from oceans and formicine ants. Other sources of emission of the two acids include anthropogenic and biogenic emissions and photochemical oxidation of precursor organic gases (Khare et al., 1997). Carboxylic acids occur in troposphere in both aqueous phase and in gas phase. Their occurrence in fog, rain water, snow and ice water, in gas phase and in aerosols has been reported by various workers. Apart from the presence of formic and acetic acids, various other monocarboxylic acids have also been detected in different areas. As for example, presence of pyruvic acid has been reported in gas phase in the tropical environment of Amazonia forest, in mid-latitude temperate area of United States, in marine areas and at high altitudes. Their concentrations are however found to be lower than that of acetic acid and formic acid. Diacids like succinic, malonic, oxalic, pthalic acids have also been found with oxalic acid being the dominant species (Chebbi & Carlier, 1996). Removal of carboxylic acids from the atmosphere is mainly associated with wet and dry deposition processes. Their removal from the atmosphere is also affected by reaction with OH radical. However, the process is relatively slower. For example, at an OH concentration of $1*10^6$ radicals cm^{-3}, the lifetime of formic acid is ~26 days. Hence, the major sink of carboxylic acids is by wet and dry deposition (Finlayson – Pitts and Pitts, 2000).



Inorganic ions in the atmosphere are responsible for the deterioration of the air quality by the scattering and absorption of radiation and also affecting the visibility. Of the diverse range of inorganic ions present, sulphate, nitrate and ammonium (SNA) constitute the most important fraction of $PM_{2.5}$. Sulphate is primarily concerned with scattering of solar radiation and thus has a cooling effect on the atmosphere. Inorganic ions contribute a major fraction to the $PM_{2.5}$ particles with a variation of about 30-50% (Liu et al., 2014). The other water soluble cations and anions that have been detected by various other groups of scientists include F^-, Cl^-, Ca^{2+}, NH_4^+, K^+, Na^+ and Mg^{2+}, NO_2^+. Analysis of water soluble sulphate, nitrate and ammonium is essential to describe the acidity of rain water. Sulphate and nitrate are formed as a result of gas to particle conversion in the atmosphere. Ammonium is formed in the atmosphere from its precursor gas ammonia and is thus important in the neutralization of acidity by reaction with sulphuric acid, nitric acid and to a lesser extent hydrochloric acid. As a result of this neutralization reaction, $(NH_4)_2SO_4$, NH_4NO_3 and NH_4Cl are formed (LianFang et al., 2015). Most of the sulphur is emitted into the atmosphere in the form of SO_2 mainly through combustion and is an important contributor in the formation of smog. A well known example is the London smog which occurred in 1954 leading to about ~4000 deaths. Further, it is necessary to examine the chemistry of sulphate and nitrate ions as they play vital roles in acid deposition (wet and dry deposition), commonly termed as the "acid rain". The important reactions highlighting the gas phase oxidation of SO_2 and NO_2 to form gaseous acids, H_2SO_4 and HNO_3 are as follows:

$$OH + SO_2 \xrightarrow{M} HOSO_2 \xrightarrow{H2O} H_2SO_4$$

$$OH + NO_2 \xrightarrow{M} HNO_3$$

The anions and cations are emitted into the atmosphere from sources such as sea spray which contain inorganic ions like Na^+, Cl^-, Ca^{2+}, Mg^{2+}, etc. and other secondary processes occurring in the atmosphere.

Metals comprise a very minute fraction of the $PM_{2.5}$ particulate matter. They are found to originate both naturally and by anthropogenic activities. The natural sources of metals are largely associated with the coarse fraction while the fine fraction consists mainly of the anthropogenic sources. The natural sources of metals include wind-blown dust, volcanic eruptions, sea salts, forest fires and emission from vegetation whereas anthropogenic emissions of metals are principally through combustion processes (Lakhani et al., 2008). A variety of metals have been detected in different parts of the world. The existence of different metals in different parts or regions can be related to the major activities being carried out in that particular location. Therefore, metals are shown to relate with the anthropogenic activities in some cases and with the crustal origin in others. For instance, a few metals such as Fe and Mn are reported to have crustal origin and are thus defined as crustal elements. Metals like Ni, V and Se have increased concentration levels in locations associated with petrochemical refining or oil processing activities. Other metals that have been analysed by researchers include Zn, Sn, Sb, Cd, Cu, As, Ba etc. that are exposed to the atmosphere through processes such as agricultural activities, metal processing units or industries, coal combustion and vehicular traffic (Zereini & Wiseman, 2010). Hugh levels of Pb concentrations in ambient air are particularly associated with the emissions from the exhausts of motor vehicles carrying leaded petrol. The importance of the study of metals lies in the fact that they have varying degrees of toxic effects on both the health and the environment. As already stated, they enter the atmosphere through a variety of sources and are then passed to the human systems. Apart from this, metals also have their effects on plants, the most probable source being the soil. Metals have significant toxicological and carcinogenic effects on human health which may be either acute or chronic. They enter the respiratory tracts causing significant lung related diseases like asthma, bronchitis and may also lead to various allergies. The toxicity of metals is also dependent on the size fraction and morphology of particles. Large particles are not capable of penetrating much deeper into the

respiratory systems and thus remain superficially in the upper respiratory tracts while the finer ones enter deep into the pulmonary system and get mixed with the blood streams causing long term effects. Their solubility into the body fluids is an important criterion in governing the level of their toxicity. After being released into the body fluids, metals lead to the production of free radicals through mechanisms like the Fenton's reaction and may cause cellular inflammation (Birmili et al., 2006).

In terms of global perspective, the concentrations and the toxic effects of the various chemical constituents of the PM fraction is largely dependent on the meteorological parameters. Meteorological factors such as wind speed, wind direction, temperature, relative humidity, solar radiation and rainfall are important contributors in defining the concentration levels, dispersion and removal of the pollutants in the ambient air. In a particular location, the pollutant concentration levels are also found to vary according to seasons. Temperature, wind speed and relative humidity, in particular, play important roles in describing the seasonal variation of concentrations within a region. Increasing temperature levels lead to the rising up of particles from the ground surface and disperse or transport them to other distant areas by the speedy winds. Such types of conditions are usually found to prevail during the summer season when the temperatures are high and heavy winds blow. A general trend is that the dispersion of pollutants to distant locations is affected by high wind speeds whereas low wind speeds lead to the build up of pollutant concentration levels. However, results from correlation studies may be obtained that contrast from the general trend (Galindo et. al., 2011). A number of scientists, for example, Giri et al., (2008) report that even the topography of the region has an influence on the pollutant concentration levels.

Source apportionment techniques have been an important tool in describing the major pollution sources and have thus helped to improve the air quality standards around the world. Techniques like Principal Component Analysis (PCA), Positive Matrix Factorization (PMF), Potential Source Contribution Function (PSCF) and Chemical Mass Balance (CMB) have been useful in the identification of various sources. Pollutants are not only limited to the local sources but may also be brought into the landmasses through long range transport and thus air mass back

trajectory models like the HYSPLIT model has become an important method to identify the long range transport of sources.

In recent years studies have been conducted both outside and in India. The main focus of such studies are simultaneous analysis of gases as well as particulate matter. This has proved to be an important step in the understanding of gas-to-particle conversion process and the formation of secondary inorganic and organic aerosols. The major gases that have been simultaneously studied are SO_2, NOx, HNO_3 and NH_3. The conversion of these gases into secondary pollutants is still not clear. The possible mechanisms for such conversions are being built up to understand their existence in the atmosphere. The formation of secondary pollutants in the atmosphere is affected by the meteorological factors and the concentrations of their precursors and other atmospheric oxidants. HCl, HONO and HNO_3 have also been studied simultaneously and these have provided important information regarding the acidity of the environment. In presence of large amounts of ammonia, these acidic gases are neutralized to form their corresponding ammonium compounds in the particulate phase.

$PM_{2.5}$ chemical characterisation and source apportionment is a very important area of atmospheric chemistry research and several studies are being conducted at various parts of the globe in this area.

LITERATURE REVIEW

Atmospheric particulate matter has lead to significant deterioration of the air quality in the past and the present trends are continuing to add to the increasing pollution worldwide. A number of studies have been conducted on the characterization of particulate matter. In the past two decades majority of the studies were focussed on the measurement and chemical characterization of total suspended particulate (TSP) (Tare et al., 2006; Rengarajan et al., 2007;Sudhir and Sarin 2008; Ram et al., 2008). However, with the vast research it has been shown that $PM_{2.5}$ particles are much more important as they are concerned with the global climatic changes, health problems and visibility degradation.

In China, increased $PM_{2.5}$ concentrations were reported during 1995 to 1996 (Wei et al., 1999). 24h PM_{10} and $PM_{2.5}$ samples collected at Hanoi in Vietnam showed that the annual mean concentrations were (87.1±73.1) μgm^{-3} for PM_{10} and (36.1± 71.3) μgm^{-3} for $PM_{2.5}$ and that the PM_{10} US National Ambient Air Quality Standards (NAAQS) was exceeded on 52 days. Also, $PM_{2.5}$ concentrations exceeded 50μgm^{-3} on 77 days (Hien et al., 2002). In India also, increased PM concentrations have been reported by various scientists (Gupta et al., 2008; Tiwari et al., 2015). Tiwari et al., 2014 performed real time analysis of particulate matter (both $PM_{2.5}$ and PM_{10}) and showed that the mean mass concentrations were 129.8± 103.4 and 222.0± 142.0 $\mu g/m^3$ which were relatively high than the NAAQS standards of India.

Particulate matter is composed of a number of chemical constituents which include Organic Carbon (OC), Elemental Carbon (EC), metals, water soluble ions and Poly Aromatic Hydrocarbons (PAH). Initial studies on particulate matter have focussed mainly on the individual characterization of these species. Carbonaceous aerosols have been studied by various researchers and have been shown to have great impacts on the environment and health (Frazer, 2002). Although Black Carbon (BC) is the largest component of light absorbing aerosol, evidences support that Organic Carbon also play an important role in the absorption of light radiations at specific wavelengths (Kirchstetter & Novakov, 2004). Large amounts of organic carbon and black carbon are emitted from coal combustion and therefore studies have been carried out to determine the concentrations carbonaceous materials in particulate matter at

different sites (Zhang et al., 2008). In Italy, carbonaceous aerosols in PM_{10} were studied recently for their spatial and seasonal variability at industrial, traffic, urban, semi-rural, rural and remote locations. The results showed that the OC concentrations ranged from 1.2μgm^{-3} to 15.2 $\mu g\ m^{-3}$. The EC concentrations exhibited a larger variability, ranging from 0.1 μgm^{-3} to 5.6 μgm^{-3}, and increased more than 50 times from remote to traffic sites (Sandrini et al., 2014). A long term study conducted by Ahmed et al., 2014 at a rural site in New York showed about 32% decrease in BC concentrations in 27 years and on the annual basis about 18% contribution to the emitted BC came from wood burning. The HYSPLIT 4 air trajectory model established that the air masses blowing over Ohio River Valley and Mid-Atlantic States contributed maximum to the BC concentrations. Pollutants may be emitted into the atmosphere both naturally or by anthropogenic activities. Based on the anthropogenic or natural origin of secondary organic aerosol, a study was carried out in Los Angeles Basin which focussed on the influence of regional transport on the concentrations of biogenic and anthropogenic secondary organic carbon (SOC) in $PM_{2.5}$ OC. 40% of the annual average $PM_{2.5}$ OC mass contained anthropogenic and biogenic SOC and a distinct seasonal pattern was observed with anthropogenic SOC contributing mostly in summer while the biogenic SOC contributed mostly in the spring season. Apart from this the results also established that the biogenic SOC resulted from the transport of pollutants from outside the region while anthropogenic SOC is associated with the local sources in combination with the humid air above the ocean (Heo et al., 2015).

Organic Carbon (OC) and Elemental Carbon (EC) concentrations have been determined in total suspended particles (TSP) at a sub-urban site in India. The results reported that annual average TSP concentrations were 216.3±80.7 μg m−3. OC concentrations were found to be 25.4±19.8 μgm−3 (ranging from 2.5 to 91.0 μgm−3) while EC concentrations were 3.3±3.0 μg m−3 (ranging from 0.3 to 15.2 μgm−3) (Satsangi et al, 2012). Pachauri et al., 2013 carried out their study in $PM_{2.5}$ samples collected at traffic, rural and sub-urban sites in Agra. $PM_{2.5}$ mass concentrations were reported to be higher than the NAAQS and WHO standards. The average concentrations of OC and EC at the at the traffic, rural and sub-urban were reported to be 86.1 ± 5.2 and 19.4 ± 2.4 s, 30.3 ± 12.9 and 4.0 ± 1.5 and 44.5 ± 18.5 μg/m3 and 5.0 ± 1.4 μg/m3.

The organic fraction of carbonaceous aerosols is found to contain a significant proportion of organic acids and therefore a vast number of studies were also conducted to investigate the presence of organic acids in carbonaceous aerosols. Organic acids have been reported to be emitted directly by vegetation (Keene and Galloway, 1988; Yu et al., 1988; Talbot et al., 1990; Kavouras et al., 1998). Formic and acetic acids have been reported to be the most abundant carboxylic acids in the troposphere (Keene et al., 1995). Presence of carboxylic acids have been reported mainly in rain water (Kieber et al, 2002), in cloud water (Loflund et al., 2002) and in polar ice samples (Legrand and Saigne, 1988).

With the advances in research on particulate matter, investigations of chemical composition also included the inorganic ions. In China, in addition to carbonaceous aerosols and metals, $PM_{2.5}$ were also characterized for its ionic species, (Gu et al., 2011; Liu et. al., 2014). It was shown by Gu et al. in 2011 that the $PM_{2.5}$ levels in Tianjin exceeded 1.4 to 9.1 times of the USEPA standard levels in winter. Also, the average sulphur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR) of 0.19 established that the major source of secondary SO_4^{2-} and NO_3^- were the transformation of the gaseous SO_2 and NO_2 to the particulate phase. The recent advances in characterization of aerosols have also focused on the acidities of these particles. Aerosol acidities have been determined in China in the Pearl River Delta (PRD) region during the hazy and non-hazy days (Fu et al., 2015). The analysis of their results showed that on hazy days, $[H^+]_{total}$, $[H^+]_{insitu}$, $[HSO^-_4]$ and LWC were reported to be 0.9-2.2, 1.2-3.5, 0.9-2.0 and 2.0-3.0 times compared to the non-hazy days. From the t-test analysis, contrast between the $PM_{2.5}$ acidity on both hazy and non-hazy days was also shown when the acidity increased from high to low on the hazy days with notable increase in OM concentrations. In the same year, a study conducted in Himalayan region of India by Kuniyal et al., 2015 reported the characteristics of water soluble ions in PM_{10} particles during the episodic days. Their results showed that the ions were acidic in nature and that HNO_3 and HCl contributed slightly to the acidity. The results also showed the predominance of NH_4NO_3 and $(NH_4)_2SO_4$ at Mohal (NH_4^+/NO^-_3 is 0.29 and NH_4^+/SO_4^{2-} is 0.5) and Kothi (NH_4^+/NO^-_3 is 0.15 and NH_4^+/SO_4^{2-} is 0.28) while the airmass back

trajectories showed that during the high pollution episodic days, winds from Eastern part of India brought in pollutants.

Studies on metals have been carried out using various techniques like the X-ray fluorescence (XRF), atomic absorption spectroscopy (AAS) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Thomaidis et al., 2003 determined Pb, Cd, As and Ni concentrations in $PM_{2.5}$ particles at two sites in Athens basin (Patission Street in Athens centre and Rentis, a semi-urban and industrial area). The annual mean concentrations reported were as follows- Pb: 143ng/m3, Cd: 0.34ng/m3, Ni: 4.55ng/m3 and As: 0.79ng/m3. Source apportionment analysis showed that vehicle emissions, coal combustion and resuspended road dust contributed to Pb, As and Ni while industrial activities contributed to the emission of Cd and a portion of As. In another study, carried out at two sites (Escobedo, a traffic site and Santa Cantarina, an urban site) in Monterrey, Mexico, $PM_{2.5}$ samples were analysed for metals, OC, EC and inorganic ions using techniques like X-ray fluorescence (XRF), ion chromatography and thermal optical analysers. The enrichment factors indicated that S, Cl, Cu, Zn, Br, and Pb came from anthropogenic sources (EF>50). Ca showed a maximum mean concentration and the measured components accounted for 96% of the $PM_{2.5}$ mass. $PM_{2.5}$ was composed of 41.7% OC, 22.9% SO_4^{2-}, 12.6% NO^-_3, 11.4% crustal material and 7.4% EC. Crustal material and vehicle exhaust, industrial activity and fuel oil burning have been shown to be important pollution sources as reported by factor analysis (Martinez et al., 2012). PM_{10} and $PM_{2.5}$ have also been characterized for their metal content by Contini et al., 2014 using Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and the results reported that in accordance with the t-student test at 5% probability, at industrial site Cd, Pb and Cr in PM_{10} show an increasing trend while in the background site crustal elements like Al, Mn and Ti had a higher concentration. Al, Mn, Fe and Ti were shown to have crustal origin as their enrichment factor values were low whereas Ni and Cr in both PM_{10} and $PM_{2.5}$ were highly enriched indicating that they originated from industrial sources.

Studies on metals in India have been done to determine their morphological features. In a study carried out by Pachauri et al., 2013, the SEM-EDX analysis accounted for the presence of

biogenic, geogenic and anthropogenic particles. Further, the analysed particles were in the range of 2-70µm in size and were mostly of crustal origin. Also, aluminosilicate particles contributed a major portion of the analysed particles. In another study by Pachauri et al., 2013, carbonaceous aerosols were analysed during the episodic events. The results reported higher concentrations of OC and EC during the night. The OC and EC concentrations in $PM_{2.5}$ were found to be 22.8 ±17.1 µg/m^3 and 3.4 ±1.2 µg/m^3 while their concentrations in TSP were 42.1 ±22.6 µg/m^3 and 6.1 ±3.2 µg/m^3. Haze-fog events and dust storms played a significant role by causing an increase in concentration levels while rainfall caused the concentrations to decrease significantly. It was also reported that the carbonaceous particles had anthropogenic origin and had higher concentrations during winter as confirmed from the SEM-EDX and back trajectory analysis.

Long term exposures to particulate matter have toxicological effects on human health and have even resulted in mortality. Cao et al., 2012 related particulate pollution to daily mortality and found that OC, EC, sulphate, nitrate and ammonium were the major contributors of $PM_{2.5}$ mass. OC, EC, ammonium, nitrate, chloride ion, chlorine and nickel were found to associate significantly with total, cardiovascular and respiratory mortality and the associations were fairly strong between nitrate and total and cardiovascular mortality.

Stone et al., 2011 at a background site in Gosan, Korea demonstrated the importance of dust events in determining the size distribution of OC, EC and molecular markers. The important dust events that occurred were related to different sources of pollution in the region. These dust events were also compared with the non-dust events which were found to occur in the months of April and May. Therefore, in order to control the increasing pollution levels, identification of the sources have become an important task and in the recent years a majority of studies on chemical characterization of particulates have also focussed on the source apportionment studies. Zhang et al., 2013, studied chemical characterization of $PM_{2.5}$ and applied various source apportionment approaches such as positive matrix factorization (PMF), chemical mass balance (CMB), trajectory clustering and potential source contribution function (PSCF) to characterize $PM_{2.5}$ particles, identify and apportion the sources. Soil dust, coal combustion,

biomass burning, traffic and waste incineration emission, industrial pollution and secondary inorganic aerosols were reported to contribute annually 16, 14, 13, 3, 28 and 26% to $PM_{2.5}$ particles, as confirmed from the PMF model.

The chemistry involved in the formation of secondary pollutants through various photochemical processes and gas-to-particle conversion is still unclear. Therefore, attention has been drawn towards the simultaneous measurement of gases and particulates. In the context of such studies, Bari et al., 2003 carried out simultaneous measurements of acidic gases (HONO, HNO_3, HCl, SO_2), NH_3 and particulate SO_4^{2-} at two sites (Bronx and Manhattan) in New York City. Their results showed high correlations between the concentrations at the two sites. At Manhattan, the summer/winter ratios showed higher concentrations during the summer with the exception of HONO and SO_2 which were lower during the summer than during the winter. In a recent study by Behara et al., 2013 at Singapore based on simultaneous measurement of acidic gases, NH_3 and secondary inorganic gases, significant diurnal variations were observed for SO_2, NH_3, HONO, HCl, SO_4^{2-} and Cl^-. Also, NH_3 was present in sufficient concentrations and neutralized both H_2SO_4 and HNO_3. In India, Tiwari et al., 2014 made simultaneous and continuous measurement of $PM_{2.5}$ and PM_{10}, black carbon (BC), CO, NO and NOx for a period of two years. Their results showed higher levels of fine particles than coarse particles during all the three seasons except during the summer when fine particles were about 22% lower than the coarse particles. Other results of their analysis showed that local sources predominated as inferred from the negative correlation (-0.45) between wind speed and $PM_{2.5}$ particles and that Thar Desert served as a major source of particulate pollution (in particular, the coarse mode particles) as indicated by trajectory analysis.

Studies on complete characterization of $PM_{2.5}$ have been very rare. A study on complete characterization of fine particles has been conducted in Mumbai, India by Joseph et al., 2012. Fine particles were analysed for mass closure studies and the analysed chemical constituents included carbonaceous aerosols, ions and metals. The results reported OC contributed 30% at control site (C), 34% at Kerb site (K), 35% at residential (R) and 31% at industrial site (I) while EC contributed 7%, 11%, 9% and 8% at C, K, R and I sites. Enrichment factor established that

Al and Ti had crustal origin as their EF values were low (<10) while Ca, Fe, Mn, K and Cr originated from natural sources and construction activities (10>EF<1000). On the other hand, Pb and Zn had anthropogenic sources (EF>1000).

In India, systematic studies on complete characterization of $PM_{2.5}$ with respect to carbonaceous aerosols, ions (including organic ions) and metals with seasonal and spatial variation are not available. Only one study by Joseph et al., 2012 reports characterization of $PM_{2.5}$ from Mumbai with respect to carbonaceous aerosols, ions and metals (organic acids not reported). Hence, the present study is planned to fill this lacunae. The present study aims at characterizing $PM_{2.5}$ for chemical composition with respect to seasonal and spatial variation including carbonaceous aerosols, ions and metals. It is also proposed to elucidate the sources using statistical methods and backward trajectory analysis.

OBJECTIVES

The present study is being carried out with the following objectives:

1. $PM_{2.5}$ samples collected at two sites (sub-urban and rural) will be analysed for organic carbon and elemental carbon.
2. To determine the major cations (Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+) and anions (Cl^-, NO_3^-, SO_4^{2-}, CH_3COO^- and $HCOO^-$) in $PM_{2.5}$.
3. To quantify the metals (Fe, Ni, Cd, Cu, Zn, Mn, Pb and Cr) by AAS (graphite method) and determine the surface morphology by SEM-EDX method.
4. Source contribution with respect to seasonal and spatial variations will be elucidated using backward trajectory analysis and statistical methods: Correlation, Principal Component Analysis (PCA), Positive Matrix Factorization (PMF).
5. In a few representative simultaneously collected samples, gas/ aerosol partitioning will be studied at sub-urban site in each season.

MATERIALS AND METHODS

In order to study the spatial variation, the study will be carried out at two sites:

a) Suburban site

b) Rural site

Site Description

a) Suburban site: Sampling will be carried out on the roof top of Science faculty building at Dayalbagh Educational Institute located at Dayalbagh, Agra. Dayalbagh, a suburban site, is a small residential community about 10km away from the industrial sector of Agra. Vegetation predominates as a result of prevailing agricultural activities. The institute lies by the side of the road with a vehicular traffic density of about 1000 vehicles per day. The population around the area is about 25,000. The National Highway, NH-2, lies about 2 km from the sampling site. Both, Mathura oil refinery and Firozabad glass industry are located about 40km from Agra.

The city of Agra is situated in the north central region of India (27°10′N, 78°05′E, and 169 m.s.l.) with two-thirds of its peripheral boundaries (SE,W and NW) being surrounded by the Thar desert of Rajasthan. It is a semi-arid region characterised by loose, sandy, calcareous soil and a distinct monsoon season. The climate of Agra is hot and dry during the summer with a relative humidity of 25% to 40% and the temperature ranging from 25^0C to 46^0C, while the winter season features a cold weather with a relative humidity of 60% to 90% and low temperature ranging between 0.6^0C and 22^0C. The annual rainfall in Agra is about 650mm and the winds usually come from west and north-west directions.

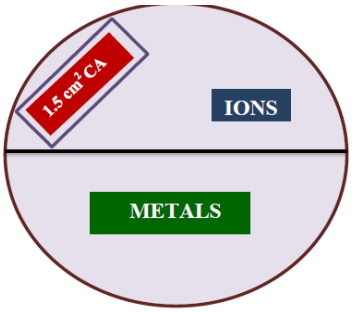
b) Rural site: Sampling will be done in a village in the north of the city away from the traffic sources and industrial activities.

Sample Collection and Measurement

$PM_{2.5}$ samples will be collected for 24h on a pre-weighed 47mm quartz fibre filters (Pallflex, Tissuquartz) using a Fine Particulate Sampler (Envirotech APM 550) operating at a flow rate of 16.6L min^{-1}. The filter papers will be pre-heated for 3h in a muffle furnace at a temperature of 800^{o}C in order to remove impurities and then equilibrated in desiccator. Weighing of the filter papers will be done on an electronic balance (Mettler, Toledo). To avoid contamination the conditioned and weighed $PM_{2.5}$ filters will be placed in cassettes and packed in polythene zip-lock bags and taken to the sampling site. After sample collection and weighing, the samples will be stored in aluminium foil and sealed in polyethylene zip-lock bags and stored in deep freezer at -4^{0}C until analysis.

Analysis

The quartz filter papers will be analysed for:



Organic Carbon (OC) and Elemental Carbon (EC)

A filter punch of about 1.5cm^2 will be used for the analysis of OC and EC. The analysis will be carried out with the help of a thermal/ optical Carbon Aerosol Analyser (Sunset Laboratory, Forest Grove, USA) using NIOSH 5040 (National Institute of Occupational Safety and Health) protocol based on Thermal-Optical Transmittance (TOT) (Birch, 1998; Birch and Cary, 1996). The procedure involves two-stages. The first stage involves the volatilization of OC from the sample in a non-oxidizing atmosphere of 100% He through a step-wise heating (340^{o}C, 500^{o}C and 615^{o}C maintained for 60s and at 870^{o}C for 90s). The thermograph thus obtained will consist of four OC fractions (OC_1, OC_2, OC_3 and OC_4). The second stage involves cooling of the oven to below 550^{o}C for 60s. A mixture of 2% oxygen and 98% helium (by volume) will then be introduced and oven temperature will then be increased step-wise to 900^{o}C (550^{o}C, 625^{o}C,

700^{o}C, 775^{o}C and 850^{o}C maintained for 45s and 900^{o}C for 120s). The thermograph will show pyrolysed carbon (PC) and three EC fractions (EC_1, EC_2 and EC_3).

The pyrolysed fraction is determined when the optical-transmittance returns to its initial value which serves as a split line between OC and EC. Thus, OC and EC components are corrected for charring of hydrocarbons due to heating producing the pyrolyzed carbon (PC) in the first-step. The OC is operationally defined as (OC_1 + OC_2 + OC_3 + OC_4 + PC) and EC is defined as (EC_1 + EC_2 + EC_3 − PC). The evolved carbon fractions will then be oxidized to CO_2, reduced to CH_4 and finally quantified using Flame Ionization Detector (FID) at 125^{o}C. A fixed volume of 5% methane in helium will be injected at the end of every analysis as an internal standard to monitor the efficiency of FID while sucrose will be used as an external standard to ascertain the conversion efficiency of CO_2 to CH_4.

Standardization of OCEC Lab Instrument will be done using a sucrose solution (3.2 μg μl^{-1}). For quality control, the analyzer will be calibrated using a blank punch of pre-heated quartz fibre filter and standard sucrose solution every day. Sampled quartz filter papers will also be analyzed similarly for blank corrections.

Ion Analysis

Major organic (CH_3COO^- and $HCOO^-$) and inorganic (F^-, Cl^-, NO_3^- and SO_4^{2-}) anions and major cations (NH_4^+, Na^+, K^+, Mg^{2+} and Ca^{2+}) will be determined by using Dionex ICS 1100 Ion Chromatograph system (Dionex Corp, Sunnyvale, CA). For cation analysis, filter paper will be extracted by sonicating with DI water for 45 min and analysis will be performed using 20mM Methane Sulfonic Acid as an eluent. The system will be equipped with guard column (CG12A), analytical column (CS12A) and cation self-regenerating suppressor (CSRS 300 4mm). The anions will be extracted using DI water and the system will be equipped with guard column (AS11A), analytical column (AS11) and anion self-regenerating suppressor (ASRS-ULTRA 4mm). 6mM NaOH will be used as an eluent for F^-, Cl^-, NO_3^-, SO_4^{2-} and 0.03mM NaOH will be used as an eluent for organic ions (CH_3COO^- and $HCOO^-$). Blank corrections will be made using similar procedures.

Analysis of Metals

Two methods will be utilized for the assessment of the metals: Atomic Absorption Spectroscopy (AAS) and SEM-EDX. Following eight metals will be identified: Fe, Ni, Cd, Cu, Zn, Mn, Pb and Cr.

a) Atomic Absorption Spectroscopy (AAS)

After sampling, the filter paper will be placed in 100ml Teflon beakers, previously soaked in 20% (v/v) HNO_3 for 4h and rinsed thoroughly with DI water. 3ml of HNO_3 will then be added and the beakers will be covered with watch glass. The contents will be heated on a hot plate in a fume hood. The digestion of the samples will be continued until the acid nearly evaporates. The beakers and the watch glasses will be allowed to cool. 2 ml HNO_3 will then be added and heating continued again to near dryness. 1ml of hydrofluoric acid will then be used to dissolve any particles present followed by gentle heating to near dryness. This dissolves the filter paper and all solid material. The dissolved sample will be cooled and about 10ml DI water will be added. The sample will be transferred to 25ml volumetric flasks and the volume made up with acidified DI water (1% HCl and 0.7% HNO_3) before filtering to remove silicates and other insoluble materials. Finally the samples will be placed in plastic containers and stored in a refrigerator at 4^oC until analysis. Analysis will then be made using Graphite furnace AAS (GFAAS) of the make ANALYTIK JENA ZEENIT 700 and hollow cathode lamps will be used.

b) SEM-EDX Analysis

Aerosol samples will be analyzed by SEM-EDX. The SEM-EDX analysis will be carried out with the help of computer controlled field emission scanning electron microscope SEM equipped with an energy dispersive X-ray system. The dry and loaded quartz fibre filter papers will be punched in $1mm^2$ from the centre of each sample. All the samples will be mounted on plastic stubs for gold coating. A very thin film of gold (Au) will be deposited on the surface of each sample using vacuum coating unit called Gold Sputter Coater (SPI-MODULE) which can prepare 6 samples at a time. The fine coating of gold makes the samples electrically conductive. The samples will then be placed in the corner of SEM-EDX chamber. EDX analysis will be

carried out at each analysis point and the elements present will be measured both qualitatively and quantitatively. The EDX spectra of blank quartz fibre filter will also be obtained.

Simultaneous sampling of Gas and Aerosol

Simultaneous gaseous samples will be collected using an impinger (Vayubodhan) while the aerosol samples will be collected using Fine Particulate Sampler (Envirotech APM 550). Analysis of gas and aerosol samples will be made using UV-visible spectrophotometer (SHIMADZU UV-1800) and Dionex ICS 1100 Ion Chromatograph system (Dionex Corp, Sunnyvale, CA).

Back Trajectory Analysis

The air mass back-trajectory analysis will be performed using the National Oceanic and Atmospheric Administration (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model which is based on the GDAS global wind field developed by NOAA/ ARL (Draxler and Rolph, 2003).

REFERENCES

Ahmed T, Dutkiewicz V A, Khan A J, Husain L; Long Term Trends in Black Carbon Concentrations in the Northeastern United States. *Atmos. Res. 137*, 49–57, 2014.

Bari A, Ferraro V, Wilson L R, Luttinger D, Husain L; Measurements of Gaseous HONO, HNO_3, SO_2, HCl, NH_3, Particulate Sulfate and $PM_{2.5}$ in New York, NY. *Atmos. Environ. 37*, 2825–2835, 2003.

Behera S N, Betha R, Balasubramanian R; Insights into Chemical Coupling among Acidic Gases, Ammonia and Secondary Inorganic Aerosols. *Aerosol and Air Quality Research 13*, 1282–1296, 2013.

Birch M E; Analysis of Carbonaceous Aerosols: Interlaboratory Comparison. *Analyst 123*, 851–857, 1998.

Birch M E & Cary R A; Elemental Carbon-Based Method for Monitoring Occupational Exposures to Particulate Diesel Exhaust: Methodology and Exposure Issues. *Analyst 121*, 1183–1190, 1996.

Birmili W, Allen A G, Bary F, Harrison R M; Trace Metal Concentrations and Water Solubility in Size-Fractionated Atmospheric Particles and Influence of Road Traffic. *Environ. Sci. Technol. 40*, 1144–1153, 2006.

Cao J, Xu H, Xu Q, Chen B, Kan H; Fine Particulate Matter Constituents and Cardiopulmonary Mortality in a Heavily Polluted Chinese City. *Environ. Health Perspect. 120*, 373–378, 2012.

Chebbi A & Carlier P; Carboxylic Acids in the Troposphere, Occurrence, Sources, and Sinks: A Review. *Atmos. Environ. 30*, 4233–4249, 1996.

Contini D, Cesari D, Donateo A, Chirizzi D, Belosi F; Characterization of PM_{10} and $PM_{2.5}$ and their Metals Content in Different Typologies of Sites in South-Eastern Italy. *Atmosphere 5*, 435–453, 2014.

Draxler R R & Rolph G D; HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory). NOAA Air Resources Laboratory, Silver Spring, MD. Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/ready/hysplit4.html).

Finlayson-Pitts, Pitts B J; Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications. *Academic Press*, San Diego, CA, 2000.

Frazer L; Seeing through Soot. *Environ. Health Perspect. 110*, A471–A473, 2002.

Fu X, Guo H, Wang X, Ding X, He Q, Liu T, Zhang Z; $PM_{2.5}$ Acidity at a Background Site in the Pearl River Delta Region in Fall-Winter of 2007–2012. *Journal of Hazardous Materials 286*, 484–492, 2015.

Galindo N, Varea M, Gil-Moltó J, Yubero E, Nicolás J; The Influence of Meteorology on Particulate Matter Concentrations at an Urban Mediterranean Location. *Water, Air, and Soil Pollution 215*, 365–372, 2011.

Gerasopoulos E, Kouvarakis G, Babasakalis P, Vrekoussis M, Putaudb J P, Mihalopoulos N; Origin and Variability of Particulate Matter (PM_{10}) Mass Concentrations over the Eastern Mediterranean. *Atmos. Environ. 40*, 4679–4690, 2006.

Giri D, Murthy K, Adhikary P R; The Influence of Meteorological Conditions on PM_{10} Concentrations in Kathmandu Valley. *Int. J. of Environmental Res. 2*, 49-60, 2008.

Gu J, Bai Z, Li W, Wu L, Liu A, Dong H, Xie Y; Chemical Composition of $PM_{2.5}$ during Winter in Tianjin, China. *Particuology 9*, 215–221, 2011.

Gupta A K, Karar K, Ayoob S, John K; Spatio-Temporal Characteristics of Gaseous and Particulate Pollutants in an Urban Region of Kolkata, India. *Atmos. Res. 87*, 103–115, 2008.

Heo J, de Foy B, Olson M R, Pakbin P, Sioutas C, Schauer J J; Impact of Regional Transport on the Anthropogenic and Biogenic Secondary Organic Aerosols in the Los Angeles Basin. *Atmos. Environ. 103*, 171–179, 2015.

Hien P D, Bac V T, Tham H C, Nhan D D, Vinh L D; Influence of Meteorological Conditions on $PM_{2.5}$ and $PM_{2.5\text{-}10}$ Concentrations during the Monsoon Season in Hanoi, Vietnam. *Atmos. Environ. 36*,3473–3484, 2002.

Joseph A E, Unnikrishnan S, Kumar R; Chemical Characterization and Mass Closure of Fine Aerosol for Different Land Use Patterns in Mumbai city. *Aerosol and Air Quality Research 12*, 61–72, 2012.

Kavouras I G, Mihalopoulos N, Stephanou E G; Formation of Atmospheric Particles from Organic Acids Produced by Forests. *Nature 395*, 683–686, 1998.

Keene W C & Galloway J N; The Biogeochemical Cycling of Formic and Acetic Acids Through the Troposphere: An Overview of Current Understanding. *Tellus 40 B*, 322-334, 1988.

Keene W C, Mosher B W, Jacob D J, Munger W, Talbot R W, Artz R S, Maben J R, Daube B C, Galloway J N; Carboxylic Acids in Clouds at a High-Elevated Forested Site in Central Virginia. *Journal of Geophysical Research 100*, 9345-9357, 1995.

Khare P, Satsangi G S, Kumar N, Kumari K M, Srivastava S S; HCHO, HCOOH and CH_3COOH in Air and Rain Water at a Rural Tropical Site in North Central India. *Atmos. Environ. 31*, 3867 3875, 1997.

Khare P, Kumar N, Kumari K M, Srivastava S S; Atmospheric Formic and Acetic Acids: An Overview. *Reviews of Geophysics 27*, 227–248, 1999.

Kieber R J, Peake B, Willey J D,Avery G B; Dissolved Organic Carbon and Organic Acids in Coastal New Zealand Rainwater. *Atmos. Environ. 36*, 3557–3563, 2002.

Kirchstetter T W & Novakov T; Evidence that the Spectral Dependence of Light Absorption by Aerosols is Affected by Organic Carbon. *Journal of Geophysical Research 109*, doi:10.1029/2004JD004999, 2004.

Kuniyal J C, Sharma M, Chand K, Mathela C S; Water Soluble Ionic Components in Particulate Matter (PM_{10}) during High Pollution Episode Days at Mohal and Kothi in the North-Western Himalaya, India. *Aerosol and Air Quality Research 15*, 529–543, 2015.

Lakhani A, Parmar R S, Satsangi G S, Prakash S; Size Distribution of Trace Metals in Ambient Air of Agra. *Indian Journal of Radio & Space Physics 37*, 434–442, 2008.

Legrand M & Saigne C; Formate, Acetate and Methanesulfonate Measurements in Antarctic Ice: Some Geochemical Implications. *Atmos. Environ. 22*, 1011-1017, 1988.

LianFang W, JingChun D, JiHua T, YongLiang M A, KeBin H, ShuXiao W, XiaoFeng H, YuanXun Z; Gas-to-particle Conversion of Atmospheric Ammonia and Sampling Artifacts of Ammonium in Spring of Beijing. *Science China Earth Sciences 58*, 345–355, 2015.

Liu G, Li J, Wu D, Xu H; Chemical composition and Source Apportionment of the Ambient $PM_{2.5}$ in Hangzhou, China. *Particuology 18*, doi:10.1016/j.partic.2014.03.011, 2014.

Loflund M, Kasper-Giebl A, Schuster B, Giebl H, Hitzenberger R, Puxbaum H; Formic, Acetic, Oxalic, Malonic and Succinic Acid Concentrations and their Contribution to Organic Carbon in Cloud Water. *Atmos. Environ. 36*, 1553–1558, 2002.

Martinez M A, Caballero P, Carrillo O, Mendoza A, Mejia G M; Chemical Characterization and Factor Analysis of $PM_{2.5}$ in Two Sites of Monterrey, Mexico. *Journal of the Air & Waste Management Association 62*, 817–827, 2012.

Pachauri T, Satsangi A, Singla V, Lakhani A, Kumari K M; Characteristics and Sources of Carbonaceous Aerosols in PM2.5 during Wintertime in Agra, India. *Aerosol and Air Quality Research 13*, 977–991, 2013.

Pachauri T, Singla V, Satsangi A, Lakhani A, Kumari K M; Characterization of Carbonaceous Aerosols with Special Reference to Episodic Events at Agra, India. *Atmos. Res. 128*, 98–110, 2013.

Pachauri T, Singla V, Satsangi A, Lakhani A, Kumari K M; SEM-EDX characterization of individual coarse particles in Agra, India. *Aerosol and Air Quality Research 13*, 523–536, 2013.

Ram K, Sarin M M, Hegde P; Atmospheric Abundances of Primary and Secondary Carbonaceous Species at Two High-Altitude Sites in India: Sources and Temporal Variability. *Atmos. Environ. 42*, 6785–6796, 2008.

Ram K & Sarin M M; Atmospheric Carbonaceous Aerosols from Indo-Gangetic Plain and Central Himalaya: Impact of Anthropogenic Sources. *Journal of Environmental Management 148*, 153–163, 2015.

Rengarajan R, Sarin M M, Sudheer A K; Carbonaceous and Inorganic Species in Atmospheric Aerosols During Wintertime over Urban and High Altitude Sites in North India. *Journal of Geophysical Research 112*, 1-16, 2007.

Safai P D, Raju M P, Maheshkumar R S, Kulkarni J R, Rao P S P, Devara P C S; Vertical Profiles of Black Carbon Aerosols over the Urban Locations in South India. *Science of the Total Environment 431*, 323–331, 2012.

Sandrini S, Fuzzi S, Piazzalunga A, Prati P et al; Spatial and seasonal variability of carbonaceous aerosol across Italy. *Atmospheric Environment 99*, 587–598, 2014.

Satsangi A, Pachauri T, Singla V, Lakhani A, Kumari K M; Organic and Elemental Carbon Aerosols at a Suburban Site. *Atmos. Res. 113*, 13–21, 2012.

Stone E A, Yoon S C, Schauer J J; Chemical Characterization of Fine and Coarse Particles in Gosan, Korea during Springtime Dust Events. *Aerosol and Air Quality Research 11*, 31–43, 2011.

Sudheer A K & Sarin M M; Carbonaceous Aerosols in MABL of Bay of Bengal: Influence of Continental Outflow. *Atmos. Environ. 42*, 4089–4100, 2008.

Talbot R W, Andreae M O, Berresheim H, Jacob D J, Beecher K M; Sources and Sinks of Formic, Acetic and Pyruvic Acids over Central Amazonia. 2. Wet Season. *Journal of Geophysical Research 95*, 16799-16811, 1990.

Tare V, Tripathi S N, Chinnam N, Srivastava A K, Dey S, Manar M, Kanawade V P, Agarwal A, Kishore S, Lal R B, Sharma M; Measurements of Atmospheric Parameters during Indian Space Research Organization Geosphere Biosphere Program Land Campaign II at a Typical Location in the Ganga Basin: 2. Chemical Properties. *Journal of Geophysical Research 111*, 1-14, 2006.

Thomaidis N S, Bakeas E B, Siskos P A; Characterization of Lead, Cadmium, Arsenic and Nickel in $PM_{2.5}$ Particles in the Athens Atmosphere, Greece. *Chemosphere 52*, 959–966, 2003.

Tiwari S, Bisht D S, Srivastava A K, Pipal A S, Taneja A, Srivastava M K, Attri S D; Variability in Atmospheric Particulates and Meteorological Effects on their Mass Concentrations over Delhi, India. *Atmos. Res. 145-146*, 45-56, 2014.

Tiwari S, Pandithurai G, Attri S D, Srivastava A K, Soni V K, Bisht D S, Kumar V A, Srivastava M K; Aerosol Optical Properties and their Relationship with Meteorological Parameters during Wintertime in Delhi, India. *Atmos. Res. 153*, 465–479, 2015.

Wei F, Teng E, Wu G, Hu W, Wilson W E, Chapman R S, Pau J C, Zhang J; Ambient Concentrations and Elemental Compositions of PM_{10} and $PM_{2.5}$ in four Chinese cities. *Environ. Sci. Technol. 33*, 4188-4193, 1999.

Yu S, Gao C, Cheng Z, Cheng X, Cheng S, Xiao J, Ye W; An Analysis of Chemical Composition of Different Rain Types in ‘‘Minnan Golden Triangle’’ Region in the Southastern Coast of China. *Atmos. Res. 47–48*, 245–269, 1998.

Zereini F & Wiseman C L S; Urban Airborne Particulate Matter (Environmental Science and Engineering). *Springer*, London, NY, 2010.

Zhang Y, Schauer J J, Zhang Y, Zeng L, Wei Y, Liu Y , Shao M; Characteristics of Particulate Carbon Emissions from Real-World Chinese Coal Combustion. *Environ. Sci. Technol. 42*, 5068–5073, 2008.

Zhang R, Jing J, Tao J, Hsu S C, Wang G, Cao J, Lee C S L, Zhu L, Chen Z, Zhao Y, Shen Z; Chemical Characterization and Source Apportionment of $PM_{2.5}$ in Beijing: Seasonal Perspective. *Atmospheric Chemistry and Physics 13*, 7053–7074, 2013.